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HIGH ENERGY DENSITY LITHIUM PRIMARY CELLS USING
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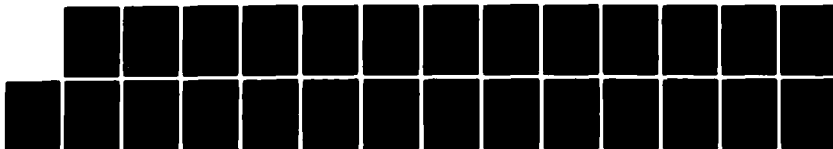
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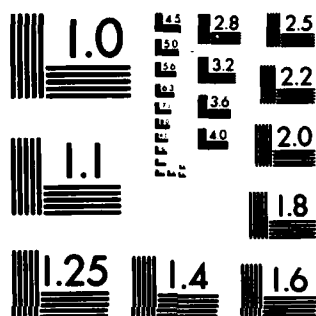
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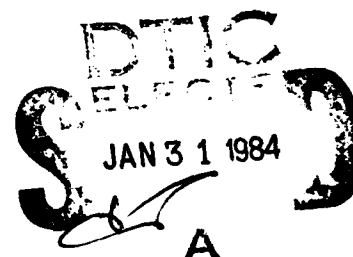
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HIGH ENERGY DENSITY LITHIUM PRIMARY CELLS
USING NITROGEN CONTAINING POLYMER POSITIVES

Prepared by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) It was proposed that nitrogen-containing, conductive polymers could be useful as cathode materials in lithium primary cells. The research consisted of the synthesis and evaluation of polymers and of monomeric model compounds. Polyaniline (aniline black) was identified as a promising cathode material. Generally, the desired polymers proved to be difficult to synthesize, in part due to their unique properties.		

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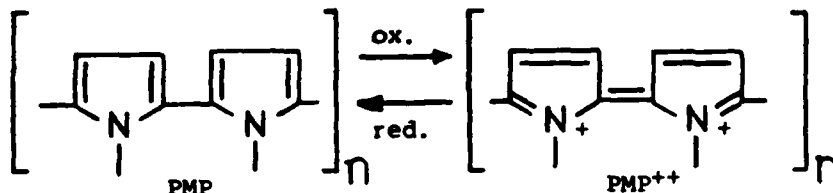
1.0 INTRODUCTION

Recent reports indicate that conjugated polymers may be useful as cathode materials in Li batteries. Polyacetylene (PA) is probably the most widely publicized of these materials. Unfortunately PA appears to be unstable, reactive with organic electrolytes, and poorly reversible.

We have suggested that a polymer electrode material would be less reactive if the charges were stabilized on heteroatoms, particularly nitrogen. A positive charge would be stored in the form of an ammonium ion. In a high energy density Li cell such a material would require a low equivalent weight counter ion (e.g., F^- or Cl^-). Currently only high equivalent weight anions have been used with the secondary Li electrode. Therefore these materials are chiefly of interest for use in primary cells although they should operate reversibly.

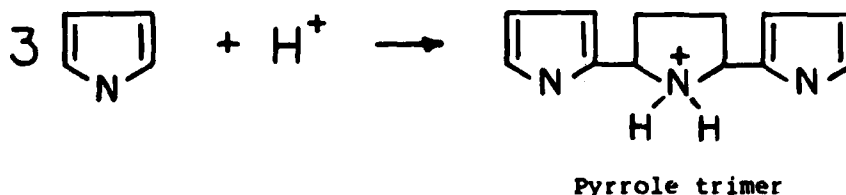
2.0 POLYMERIC CATHODES

A polymer which might be expected to exemplify charge stabilization by nitrogen is poly-N-methylpyrrole (PMP). This material is electronically conductive and might store one charge per nitrogen atom.



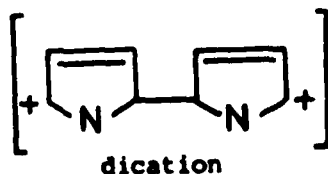
An additional, seductive attraction of this polymer is that it can be formed easily on an electrode via electrooxidation of N-methylpyrrole. Unfortunately in our hands, and in agreement with other reports, only a fraction (<20%) of the theoretical charge can be obtained experimentally (1).

One explanation for this poor redox behavior may be that the structure of the polymer formed is much less perfect than described above. Recent XPS studies indicate that every third pyrrole ring in polypyrrole (PB) is nonideal (2). This may be rationalized by examining the reaction of acid with pyrrole to make "pyrrole trimer" (3).

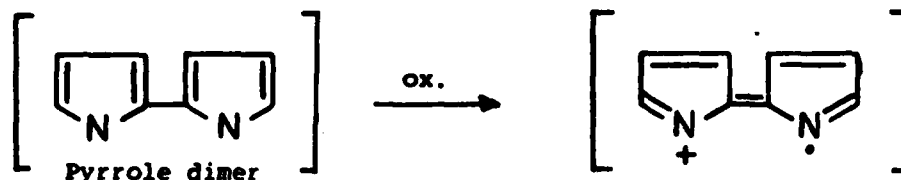


The idealized electrosynthetic route to polypyrrole (PP) may be complicated by the reaction of pyrrole with the acid formed in the synthesis. This might produce insulating links in the polymer chain like the pyrrolidinium ring in "pyrrole trimer". This material would be expected to be insoluble.

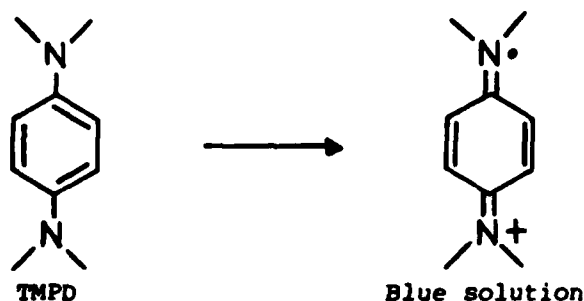
An alternative explanation for the poor redox behavior involves the intermediate dication (shown below) formed by electrooxidation. This intermediate might react with additional pyrrole before the elimination of H^+ . This would disrupt the conjugation, and therefore the conductivity, in the chain.



If, on the other hand, two protons were eliminated; then pyrrole dimer would be formed. Our investigations have led us to believe that this pyrrole dimer would form a radical cation which may be too stable and soluble to further polymerize on an electrode.



Certainly this is true for a similar molecule, tetramethyl phenylenediamine (TMPD). When TMPD is oxidized on an electrode, a blue solution of its radical-cation is formed.



Based on the above observations the poor performance of PP and PMP may be explained as resulting from defects in the polymer structure and particularly in the conjugated backbone. These defects may be important in allowing the synthesis of the polymer on an electrode. Recently, a reference has been made to the preparation of PMP by a chemical method which might be expected to make polymers which are more defect free (4). This material has been found soluble.

We hypothesize that conditions which allow polymer synthesis on an electrode may not be the best conditions for making a conductive cathode material. Or alternatively, the defects in the polymer which suppress its redox capabilities are associated with the ability to form the material on an electrode. In such materials it might be expected that some modification of the polymer would be necessary after synthesis to make it useful as a cathode material.

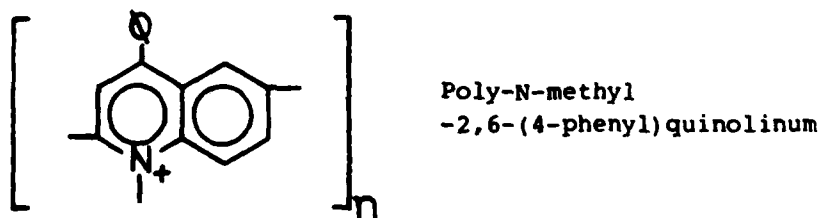
In our work both electrochemical and chemical syntheses of polymer materials were investigated. Generally the electrochemical approaches were unsuccessful. Either the monomer was too unreactive or the oxidized product too stable and soluble. Much of our effort was employed in attempts at chemical synthesis.

2.1 Properties of Polymer Cathodes

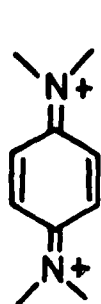
Characteristics necessary in a cathode material include:

- Stability to electrolyte.
- High voltage vs. Li
- Low equivalent weight (EW).
- Sufficient electronic conductivity ($>10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}$).
- Insoluble and wettable (ionically conductive)

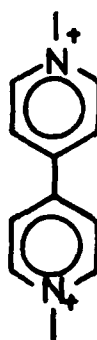
The class of compounds chosen for study, i.e., nitrogen stabilized polymers, should meet the first two requirements. The voltage of the oxidized species (vs. Li) should be large, but not so large as to be reactive with common organic electrolytes. Polymeric examples include PMP⁺ (3.5V vs. Li) and poly-N-methyl-2,6-(4-phenyl)quinolinium (2.3V vs. Li) (6)



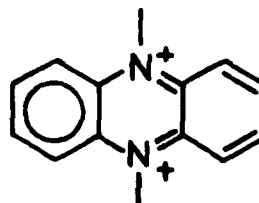
Non-polymeric model compounds are: TMPD⁺⁺ (3.8V vs. Li) (7), methyl viologen⁺⁺ (MV⁺⁺) (2.7V vs. Li) and 5,10-dimethyl phenazine⁺⁺ (DMP⁺⁺) (4.0V vs. Li) (7).



TMPD⁺⁺
E.W.82



MV⁺⁺
E.W.93



DMP⁺⁺
E.W.105

Notice that TMPD⁺⁺ and DMP⁺⁺ become aromatic on reduction unlike MV⁺⁺ which loses its aromaticity on reduction. This results in higher reduction potentials in TMPD⁺⁺ and DMP⁺⁺ than in MV⁺⁺. The ~1V difference in potentials can be attributed to aromatic stabilization.

The model compounds above appear to be stable in the absence of H_2O , and MV^{++} appears stable to H_2O as well. Additionally PMP and the model compounds have sufficiently low equivalent weights to be interesting ($EW < 100$). If these monomeric units could be incorporated into a conducting polymer, the polymer could be useful as a cathode material.

It is important that the cathode in a cell has sufficient conductivity, both electronic and ionic. The ionic conductivity of organic electrolytes used in Li batteries is typically $\sim 10^{-2} \text{ ohm}^{-1}\text{cm}^{-1}$. The ionic conductivity in a polymeric electrode would result chiefly from the electrolyte wetting the polymeric material. In a polymeric cathode material ions must be accessible to all the polymer down to a molecular level. Synthesizing polymeric cathode materials which are electronically conductive while simultaneously wetted and insoluble may be difficult.

The cathode material must be capable of transporting electrons as readily as ions. The ability of the electrode to carry electrons can be improved by the addition of carbon. If the particles in the cathode are small this will increase the effective conductivity of the polymer by 10^1 or 10^2 . This means that the polymer could have an electronic conductivity as little as $\sim 10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}$ and be useful in a battery. However, polymers with lower conductivities are not interesting.

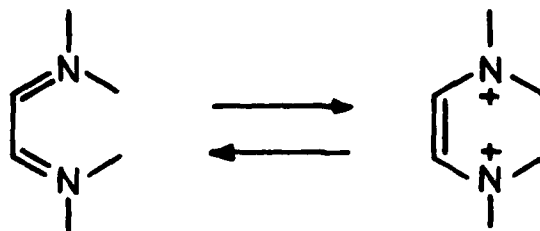
The early literature on semiconducting polymers is plentiful (8). Most of the conductivities quoted, however, are too low to be useful in a cathode material. More recently there has been an increased realization that these conductivities can be augmented dramatically by doping the polymers (9). It has also been shown that the amount of doping necessary to increase the conductivity dramatically is small as compared to the theoretical storage capacity of the electrode (6,10). Therefore, most of the capacity of the electrode is electrically accessible before the conductivity drops due to loss of doping.

When reviewing the semiconductor polymer literature it is necessary to consider the possibility of vastly increased conductivity due to doping during charge or discharge. There is a question as to whether doping can be maintained on stand or will disappear into redox traps (defects).

2.2 Choice of Polymer

A polymer might have many of the desirable characteristics as cathode materials except for a low equivalent weight (6,10). Although such a material would be very interesting, it would not be useful as a high energy density cathode. It also might be that the lessons learned in this exercise might not extrapolate to low equivalent materials. Therefore in this project we concentrated on polymers which theoretically should fulfill all the requirements stated in the previous section including low equivalent weight. This adds appreciably to the difficulty of the synthesis.

The selection of polymers was a compromise between ease of synthesis and potential properties as a cathode material. The essential structural elements are a coupled nitrogen (heteroatom) redox pair and a conjugated backbone.



Coupled nitrogen
Redox pair

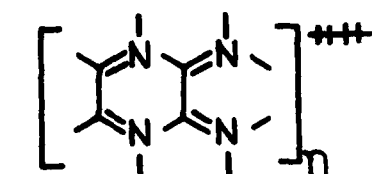
Much literature work was done in an effort to identify a particular polymer which would be accessible synthetically and yet contain the essential cathode characteristics. Our work on this project reflects the difficulty encountered in this pursuit.

The particular choice of polymer depends on the synthetic route attempted. When attempting to synthesize a polymer on an electrode surface, a monomer is chosen so that the insoluble product would be very close in structure to the desired cathode material. This approach is a result of the recognition that after the polymer has been made, subsequent reactions would be difficult and the product nearly impossible to purify. The conductivity in a polymer would be very sensitive to purity (especially to breaks in the conjugated chain). Thus, lacking the ability to purify the polymer, reactions must occur in very high yield. This is a clear analogy to polypeptide synthesis.

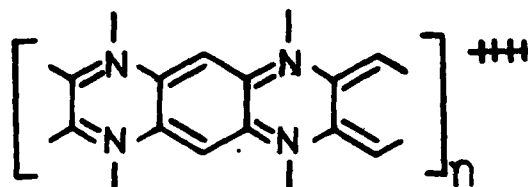
The choice of polymers for chemical synthesis was based on literature precedent and on reactions known to be quite specific for a given product. This specificity was based both on kinetic and thermodynamic considerations. The polymers chosen contain bridging nitrogen groups.

The syntheses attempted include both oligomers and polymers. The oligomers were synthesized as model compounds for the polymers and with the hope that the well-characterized oligomers might be cross-linked in a final step to convert them to insoluble polymers.

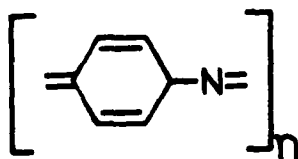
The polymers of interest were:



Methylated paracyanogen
(MPCy)



Methylated polyquinoxaline
(MPQx)



Polyaniline
Aniline black (AB)

It is indicated in the literature that oligomers of this type with up to eight nitrogen atoms might be synthesized as well characterized, soluble (in the reduced state) compounds.

The backbone of the above oligomers and polymers had been previously synthesized; however, the permethylated materials are not known. We were interested in the conductivity and electrochemistry of these materials both methylated and unmethylated.

The syntheses of these polymer materials offer some unique challenges to the synthetic organic chemist:

- Solubility. The final product must be insoluble in both oxidized and reduced states. This makes the material hard to characterize and difficult to react due to the heterogeneous nature of reactions. Ideally the synthesis would give an insoluble product only in the last step. In the case of oligomeric amines the reverse is observed. The intermediate amines, which have hydrogens bonded to the nitrogens, hydrogen-bond intermolecularly giving insoluble material. On replacement of the hydrogens by methyl groups, the amines become more soluble.

- Reactivity. The polymers would have a variety of oxidation states and the treatment of the material using common synthetic procedures can change the oxidation state in unexpected ways. The exposure of the polymer to air, water, or protic solvents may cause problems. A particular problem with the amine polymers in their oxidized states is their potential reactivity with H_2O . A synthetic sequence with the exclusion of O_2 , H_2O , and protic solvents is difficult.

• Purification. A typical organic synthetic scheme involves many intermediate purification steps. Polymer synthesis typically involves the synthesis of appropriate monomers in high purity and then the formation of the polymer in a single, well-understood step. Modification of the polymer after it is formed relies on well understood, high yield reactions to give the desired product, for purification of the polymer will be difficult. The success of a polymeric cathode material depends on its synthesis in a relatively high state of purity. That is, the structure of the polymer must be relatively well defined.

The list of synthetic difficulties goes on. It is clear that the synthesis of these polymers requires a unique set of experimental techniques and considerations.

3.0 RESEARCH

We have pursued two approaches to the synthesis of polymeric cathode material: chemical synthesis and electrochemical synthesis on an electrode. Each approach has associated with it specific types of polymers for which the approach is most appropriate. The synthetic approaches and associated polymers will be discussed.

3.1 Electrochemically Synthesized Polymers

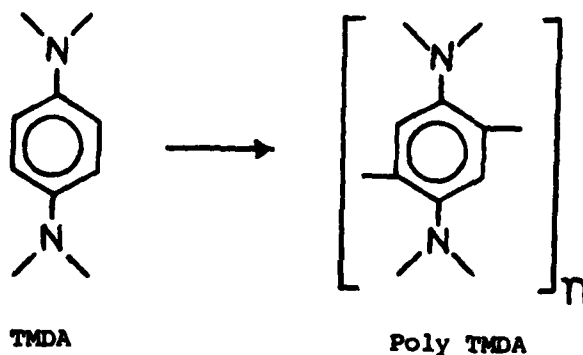
Several conductive polymers have been synthesized on electrodes. These are formed by oxidative coupling of pyrroles, thiophenes, furans, aniline, azulene and others. We found this method less useful than we had anticipated at the start of the program. A problem, in addition to those discussed earlier, is that many of the monomers one might wish to react are neither available commercially nor readily synthesized. Secondly, the films tend to separate from the electrode on cycling so that much of the advantage of "in situ" preparation is lost. The results using several monomers are summarized below.

3.1.1 N-methyl Pyrrole

This compound is polymerized easily. However, the resulting film shows much less than theoretical capacity on discharge (see earlier discussion). The recent report of the synthesis of 1-methyl-2,5-dibromopyrrole (5) should facilitate the chemical synthesis of this polymer.

3.1.2 N-containing Aromatics

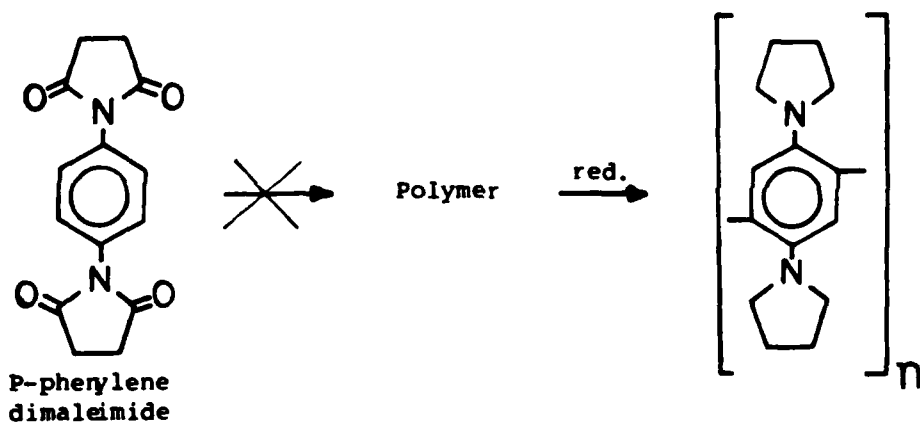
A polymer of TMDA should be nearly ideal as a polymeric cathode. Hopefully this could be formed through the oxidative coupling of TMDA or a precursor.



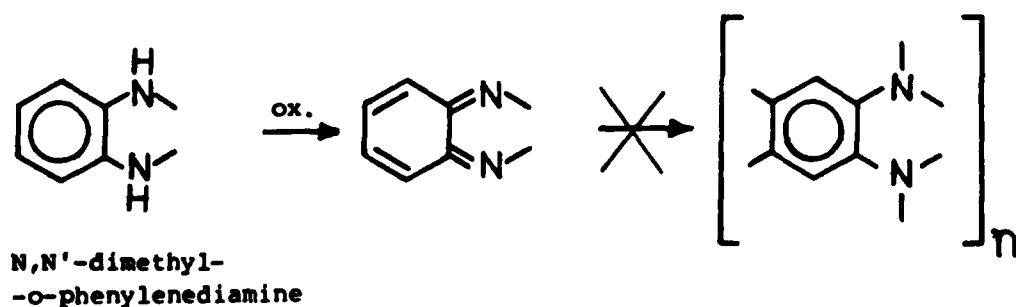
The oxidation of the monomer is known to be reversible (in the absence of H_2O) and to form a stable radical cation. In the polymer, each ring would be in conjugation in both oxidized and reduced states. Unfortunately TMDA radical cation is stable, and no polymer, only the soluble, blue radical cation, forms.

It was hoped that if the monomer could be destabilized, a polymer could be formed by the coupling of the less stable radical cations. One attempt at destabilizing the monomer consisted of protonating the amine groups with acid. This should destabilize the intermediate radical cation and cause rapid polymerization. After polymerization the film could be neutralized with base. Unfortunately no film could be formed due to the high oxidation potential of the protonated monomer.

Another approach utilized p-phenylenedimaleimide. This compound should give less stable radical cations than (TMPD), thus forming a polymer. After polymerization the imide groups would be converted to amines which should have similar properties to TMPD



Here, the oxidation potential was again too high to form the radical cation in PC. In an attempt to make a polymer with nitrogen atoms in the chain, N,N'-dimethyl-o-phenylenediamine (synthesized in house) was oxidized.



In this case some non-adherent fine solid formed around the electrode. However, the process appeared inefficient and any solid formed would be hard to isolate.

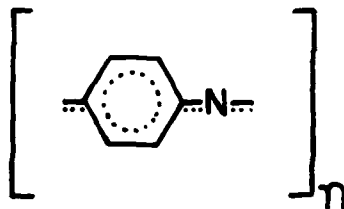
Other attempts to electropolymerize aromatic nitrogen containing compounds failed.

3.2 Chemical Synthesis

The synthesis of oligomeric and polymeric material by non-electrochemical techniques focussed on the nitrogen-containing fused aromatic systems described earlier. The essential units in these materials are shown below:

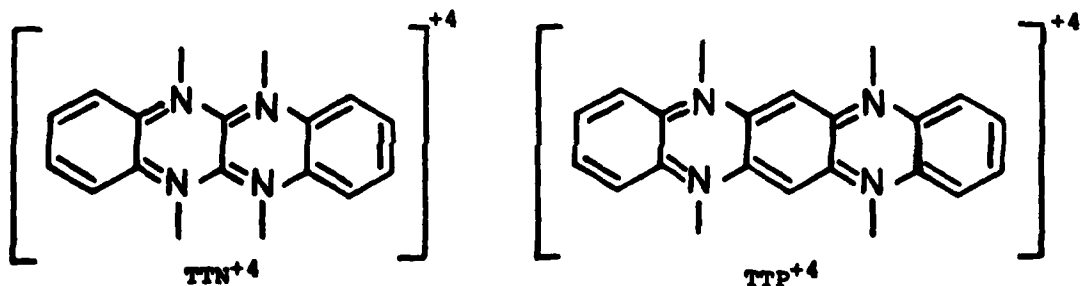


These might be called poly aza-acenes. A similar polymer which gave more promising results was polyaniline (aniline black).



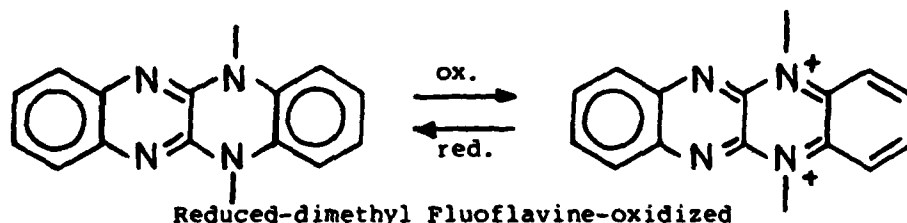
3.2.1 Oligomeric Aza-acenes

In our work two particular systems were of interest. These are tetramethyl tetraaza naphthacene (TTN) and tetramethyl tetraaza pentacene (TTP).



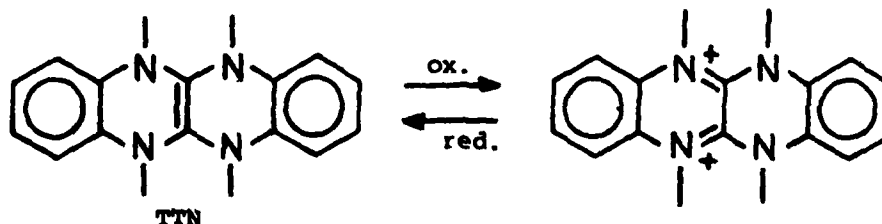
The unmethylated parent of TNN is known as Tetraaza Naphthacene [258-14-0]. In its half-reduced state it is known as fluoflavine [55977-58-7] (11). One of the dimethyl derivatives of fluoflavine has been reported (12); however, no reference to the tetramethyl derivative was found. The absence of the derivative may result from its lacking stability to oxygen and water.

The dimethyl fluoflavine is isolated in a conventional aqueous work-up with exposure to air. This compound would be expected to exist as a neutral molecule or in a positively charged oxidation state:



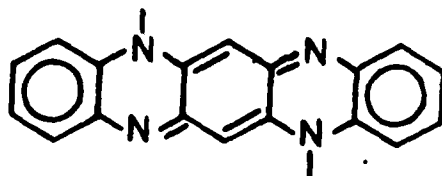
Because the product is soluble in hydrocarbons (no H-bonding is possible) the unchanged product must be formed. This product must not be air oxidized or it would be destroyed in the workup. Notice that for the oxidation to take place an aromatic ring must sacrifice its aromatic character. This implies an elevated oxidation potential, i.e., above the oxidation potential of O_2 .

In the case of the tetramethyl compound (TTN), no aromaticity loss is necessary during oxidation implying a lower oxidation potential, i.e., below the oxidation potential of O_2 . If the molecule were oxidized in aqueous solution, the methyl groups could be displaced by water. Therefore to make the tetramethyl derivative the exclusion of H_2O and air may be necessary.



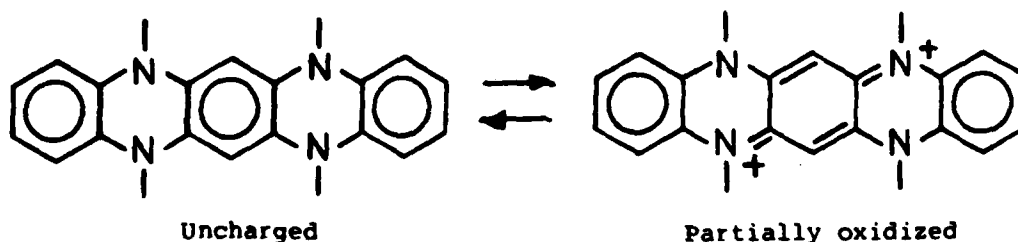
A few attempts were made by us to prepare and purify the parent fluoflavine which is quite insoluble. It became clear that making the soluble dimethylated species would be more favorable from the standpoint of purification. Unfortunately the synthesis of this material is quite difficult. Therefore the synthetic effort was shifted to a more synthetically accessible system.

The system is represented by TTP shown earlier. The structure of interest is the dimethyl derivative of dihydro-tetra-azapentacene [531-47-5] (13), shown here.



As in the above case, the dimethylated structure shows increased solubility in organic solvents (14).

The tetramethylated uncharged structure (shown below) which is totally aromatic might appear at first glance to be formed and therefore resistant to oxidation. However, it is not difficult to accept that the fully conjugated, quinone-like structure of the partially oxidized material might actually be easily formed by air oxidation and hydrolyzed in H_2O . Again, as in the above case, the tetramethyl derivative appears unknown.



It is the above work that suggests that the solubility parameters and oxidation states of the intermediates will be important considerations in the polymer syntheses. Additionally, it suggests that the conventional aqueous workup in the presence of air may not be permitted in these syntheses.

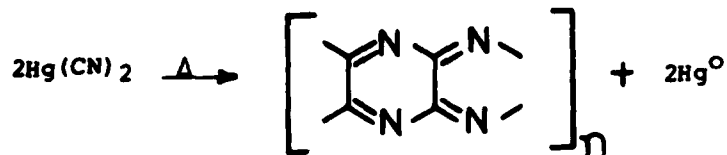
The chief synthetic target became the dimethyl tetraaza pentacene, so small quantities of this material were synthesized and purified. The purification by recrystallization was complicated by the highly colored solutions produced. In addition, the visible and UV spectra of the product are sensitive to pH.

A sample of the product was isolated in pure form by column chromatography of the acidic form of the material (blue). The product was identified by the visible spectra of the basic form (pink) with peaks at 562, 522 and 487 nm. Interestingly, when an acetic acid solution of the impure product was allowed to evaporate on a watch glass, a gold metallic color appeared. Further experimentation with this material will require scale up of the synthesis.

3.2.2 Polyaza-acenes

Our approach to the synthesis of these materials was to first make the unmethylated polymer and then methylate. There are two reasons for this. First, the parent polymers had been made previously. Secondly, even if the appropriate monomers were available commercially (which they were not) the methyl groups might be lost during the synthesis or workup. It was expected that if the parent polymer were conductive then so would be the methylated derivative.

One polymer of interest is paracyanogen (PCy) which has been known since 1816. Our approach was to form the polymer by heating $\text{Hg}(\text{CN})_2$ (15).

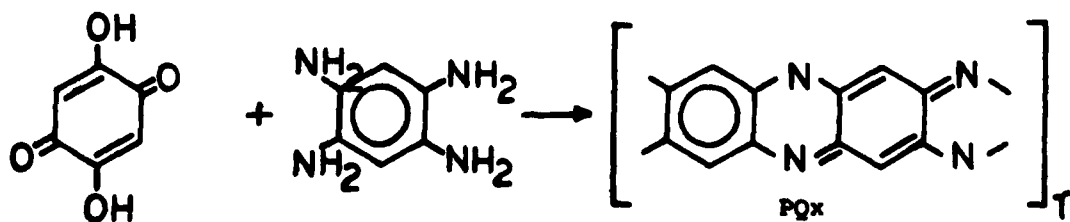


There are reports that this material has moderate electrical conductivity (16).

Attempts to prepare PCy by literature methods were complicated by the rupture of the glass reaction ampoules described in the synthetic procedure. The use of oversized ampoules and/or steel jackets minimized the problems.

Unfortunately the PCy was very poorly conductive and showed little or no electrochemical activity. The poor electrochemical activity may be due in part to insufficient wetting of the PCy powder. Subsequent attempts to reductively methylate the PCy powder yielded metallic Hg. This indicates that the black powder obtained (in at least that particular sample) contained ionic Hg. Any residual Hg in the PCy would probably disrupt the conjugation and lower the conductivity.

Synthetic difficulties led to a modified approach. An alternative to PCy is the polyquinoxaline polymers previously investigated by Stille (17). This specific polymer of interest was formed by the reaction of dihydroxybenzoquinone with tetraaminobenzene in polyphosphoric acid.



This polymer showed slight conductivity as a pressed powder ($10^{-7} \text{ ohm}^{-1}\text{cm}^{-1}$). However, again little or no electrochemical activity was observed.

When this material is prepared as described by Stille, a low yield of a black, semiconducting polymer was obtained. Difficulties were experienced in isolating the flocculant black powder from the aqueous phase. Filtration was very slow and difficult. Centrifugation may be necessary to ease the workup. Some product was undoubtedly lost in isolation. On scale-up, a brown powder was formed unlike that observed in earlier reactions. The scale-up requires further investigation.

A few attempts were made to methylate the PQX without success. Because of this and the synthetic troubles mentioned above it was decided that the research effort might better be concentrated on a material of higher equivalent weight but more synthetically accessible.

3.2.3 Polyaniline-Aniline Black (AB)

Aniline Black (AB) is made by polymerizing aniline. The structure of AB is similar to the polyaza-acenes in that the nitrogen atom is bridging between the aromatic rings. The material was synthesized by the method of Langer (18) who proposed the structure $[-N=\text{C}_6\text{H}_4=N-\text{C}_6\text{H}_4-]_n$. This polymer has no N-H hydrogens so methylation may not be necessary.

The material was obtained in good yield as a fine, black powder. This powder was extracted first by benzene, as described by Langer, and then by THF. In each case the extraction solvent became highly colored. At the end of both extractions a good yield of black powder remained. This powder is relatively conductive ($\sim 10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}$) as a pressed powder.

This material (80 mg) was formed into a pressed powder electrode (1.3 cm^2 , no carbon/Teflon) and placed in a test cell vs. Li. The OCV was 3.3V (vs. Li). The cell was discharged at 0.8 mA for 2 hrs to an OCV of 3.0V. Subsequent further discharge at 0.4 mA gave total combined discharges of 2.0 mAh. After recharging, a second discharge to 2.8V vs. Li gave 2.5 mAh output. This corresponds to an equivalent wt of 840 for the cathode material and only $\sim 43 \text{ W-hr/lb}$. However, as an initial, totally unoptimized, result this is promising.

4.0 CONCLUSION

As a result of this research effort, certain nitrogen-containing organic compounds have been identified as potential cathode materials. In preliminary tests, polyaniline has been shown to have a promising storage capacity and a cell voltage of greater than 3.0V vs. Li. Unfortunately this material was identified late in the project and only a very limited investigation was made. Further work should include structure characterization, optimization of the syntheses, and a more detailed examination of the electrochemical properties of the materials.

The early part of the project was dedicated to the synthesis of materials which should in theory give very high energy density cathodes. These syntheses proved difficult. The materials obtained were generally non-conductive, non-wettable, and inert electrochemically. However this should be viewed as a failure in the synthesis not in the concept.

For a polymer cathode material to function as designed it must have the desired molecular structure. This structure must exist in a high percentage of the material and it must have a macrostructure which allows wetting by electrolyte. Thus far the field has been dominated by polymers which are the product of serendipitous syntheses. For the field to advance greater emphasis must be placed on the synthesis of theoretically interesting polymers.

A great deal of literature work was done in an attempt to identify a particularly interesting polymer which would be synthesized in a relatively straightforward manner from commercially available materials. This attempt failed for several reasons. First many synthetic routes were inappropriate. In many cases, though a reaction was done in an aprotic solvent and under inert gas, the workup required water and could realistically be done only in air. Many of the synthetic routes were designed for individual molecules, not polymers, so product isolation required that the product be soluble. The list of examples could go on.

A second problem is that particular starting materials (monomers) were not available commercially. They could be obtained through in-house synthesis. However, this work, although relatively routine, is very time consuming.

In this project several very interesting materials were explored. Some of them show promise as cathode materials. Others, such as the azacenes have only been briefly explored. However the basic premise of the project, that a well-defined polymer with a structure of the type proposed can give a high energy density cathode, remains largely untested.

5.0 REFERENCES

1. A. F. Diaz, J. Costillo, K. K. Kanazawa, S. A. Logan, M. Salmon, and O. Fajardo, *J. Electroanal. Chem.*, 133, 233 (1982).
2. Extended abstracts of the Spring Meeting of the Electrochemical Society, May 1983, vol. 83-1, The Electrochemical Society, Pennington, NJ, Abstract No. 545 by G. B. Street, R. Geiss and P. P. Fluger.
3. H. A. Potts, and G. F. Smith, *J. Chem. Soc.*, 4018 (1957).
4. Reference (2) Abstract No. 650 by A. F. Diaz.
5. *J. Org. Chem.* 46, 2221 (1981).
6. Ref. (2) Abstract No. 544 by A. H. Schroeder, Y. S. Papir, and V. P. Kurkov.
7. C. K. Mann and K. K. Barnes, Electrochemical Reactions in Nonaqueous Systems, Marcel Dekker, NY (1970), pp. 278 and 312.
8. See Organic Semiconducting Polymers, Ed. by J. E. Katon, Marcel Dekker, NY (1968).
9. A. G. MacDiarmid and A. J. Heeger, in Molecular Metals, Ed. by W. E. Hatfield, Plenum Press, NY (1979) pp. 161.
10. P. S. Nigrey, D. MacInnes, D. P. Nairns, A. G. MacDiarmid, *J. Electrochem. Soc.*, 128, 1651 (1981).
11. P. Kuhn, S. Skrabal, and P. H. H. Fischer, *Tet.*, 24, 1843 (1968).
12. G. M. Badger, and P. J. Nelson, *Inst. J. Chem.*, 16, 445 (1963).
13. G. M. Badger, and R. Pettit, *J. Chem. Soc.*, 3211 (1951).
14. H. Wahl, M. LeBris, and D. Berkovitch, *Bull. Soc. Chim.*, 1289 (1973).
15. L. L. Bircamshaw, F. M. Tayler, and D. A. Whiffen, *J. Chem. Soc.*, 931 (1954).
16. H. Meier, Organic Semiconductors, Verlag-Chemie, Weinheim (1974), p. 240.
17. J. K. Stille and E. L. Mainen, *Marcromolecules*, 1, 36 (1968).
18. J. Langer, *Solid State Comm.*, 26, 839 (1978).

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